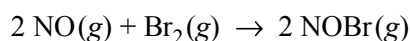


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Question 3
(9 points)



3. NO(g) reacts with Br₂(g), as represented by the equation above. An experiment was performed to study the rate of the reaction at 546 K. Data from three trials are shown in the table below.

Trial	Initial [NO] (M)	Initial [Br ₂] (M)	Initial Rate of Consumption of Br ₂ (M s ⁻¹)
1	0.10	0.20	12.0
2	0.40	0.20	192.0
3	0.10	0.60	36.0

- (a) Using the data in the table, determine the order of the reaction with respect to each of the following reactants. In each case, justify your answer.

(i) Br₂

1 st order; tripling [Br ₂] triples the rate of reaction.	One point is earned for correct order with justification.
--	---

(ii) NO

2 nd order. Quadrupling [NO] increases the rate by 16x.	One point is earned for correct order with justification.
--	---

- (b) Write the rate law for the reaction.

Rate = k [NO] ² [Br ₂]	One point is earned for the correct equation.
---	---

- (c) Determine the value of the rate constant, *k*, for the reaction. Include units with your answer.

$12.0 \text{ M s}^{-1} = k(0.10)^2(0.20)$ $k = 6.0 \times 10^3 \text{ M}^{-2}\text{s}^{-1}$	<p>One point is earned for setup.</p> <p>One point is earned for correct numerical result with correct units.</p>
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Question 3 (continued)

(d) For trial 1, determine the initial rate of formation of NOBr(g), in $M s^{-1}$.

<p>Rate of Consumption of $Br_2 = \frac{1}{2} \cdot \text{rate}$ of formation of NOBr(g)</p> $\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{NOBr}]}{\Delta t}$ $12 M s^{-1} = \frac{1}{2} \frac{\Delta[\text{NOBr}]}{\Delta t}$ $24 M s^{-1} = \frac{\Delta[\text{NOBr}]}{\Delta t}$	$\text{Rate} = -\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NOBr}]}{\Delta t}$ $12 M s^{-1} = \frac{1}{2} \frac{\Delta[\text{NOBr}]}{\Delta t}$ $24 M s^{-1} = \frac{\Delta[\text{NOBr}]}{\Delta t}$	<p>One point is earned for correct numerical result.</p>
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(e) At a later time during trial 2, the concentration of $Br_2(g)$ is determined to be 0.16 M .

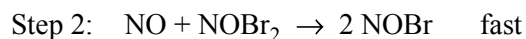
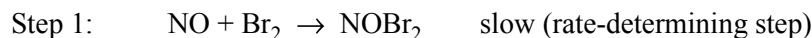
(i) Determine the concentration of NO(g) at that time.

$[Br_2]_{\text{reacting}} = [Br_2]_{\text{initial}} - [Br_2]_{\text{remaining}}$ $[Br_2]_{\text{reacting}} = 0.20 M - 0.16 M = 0.040 M$ $[NO] = 0.40 M - 0.04 M \left(\frac{2 \text{ mol NO}}{1 \text{ mol } Br_2} \right) = 0.32 M$	<p>One point is earned for correct numerical result.</p>
---	--

(iii) Calculate the rate of consumption of $Br_2(g)$ at that time.

$r = (6.0 \times 10^3 M^2 s^{-1})(0.32 M)^2(0.16 M) = 98 M s^{-1}$	<p>One point is earned for correct numerical result.</p>
--	--

A proposed two-step mechanism for the reaction is represented below.



(f) Is the proposed mechanism consistent with the rate law determined in part (b) ? Justify your answer.

<p>No. The rate law for the proposed mechanism would be 1st order in NO, but the experimental rate law is 2nd order in NO.</p>	<p>One point is earned for correct response with explanation.</p>
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Question 1
(10 points)



1. When solid ammonium chloride is heated, it decomposes as represented above. The value of K_p for the reaction is 0.0792 at 575 K. A 10.0 g sample of solid ammonium chloride is placed in a rigid, evacuated 3.0 L container that is sealed and heated to 575 K. The system comes to equilibrium with some solid NH_4Cl remaining in the container.

(a) Write the expression for the equilibrium constant for the reaction in terms of partial pressures (i.e., K_p).

$K_p = P_{\text{NH}_3} P_{\text{HCl}}$	One point is earned for correct equation.
--	---

Brackets '[]' earn zero points. Parentheses are acceptable.

(b) Calculate the partial pressure of $\text{NH}_3(g)$, in atm, at equilibrium at 575 K.

$0.0792 = P_{\text{NH}_3} P_{\text{HCl}} = x^2$ $x = 0.281 \text{ atm}$	One point is earned for correct numerical result.
--	---

(c) A small amount of $\text{NH}_3(g)$ is injected into the equilibrium mixture in the 3.0 L container at 575 K.

- (i) As the new equilibrium is being established at 575 K, does the amount of $\text{NH}_4\text{Cl}(s)$ in the container increase, decrease, or remain the same? Justify your answer.

Increase. Upon addition of $\text{NH}_3(g)$ the reaction will proceed to the left to return to equilibrium. This will result in an increase in $\text{NH}_4\text{Cl}(s)$.	One point is earned for correct choice with explanation.
--	--

Look for 'shifts left', NH_4Cl inc, because equilibrium shifts to reactants.

- (ii) After the new equilibrium is established at 575 K, is the value of K_p greater than, less than, or equal to the value before the $\text{NH}_3(g)$ was injected into the container? Justify your answer.

The same. The equilibrium constant is unaffected by change in concentration or pressure; only changes in temperature affect K .	One point is earned for correct choice with explanation.
---	--

(d) When the temperature of the container is lowered to 500 K, the number of moles of $\text{NH}_3(g)$ in the container decreases. On the basis of this observation, is the decomposition of $\text{NH}_4\text{Cl}(s)$ endothermic or exothermic? Justify your answer.

Endothermic. A decrease in T causes a reaction originally at equilibrium to proceed in the exothermic direction. Since the decrease in T in this case causes the reaction to proceed toward reactants, the forward reaction must be endothermic.	One point is earned for correct choice with explanation.
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Question 1 (continued)

In another experiment, 20.00 mL of 0.800 M $\text{NH}_4\text{Cl}(aq)$ is prepared. The ammonium ion reacts with water according to the equation $\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)$.

- (e) Calculate the value of the equilibrium constant for the reaction of the ammonium ion with water. (At 25°C the value of K_b for NH_3 is 1.8×10^{-5} .)

$K_a = K_w/K_b = (1.00 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$	One point is earned for correct numerical result.
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- (f) A solution is prepared by mixing 20.0 mL of 0.800 M $\text{NH}_3(aq)$ with 20.0 mL of 0.800 M $\text{NH}_4\text{Cl}(aq)$. Assume that volumes are additive.
- (i) Is the solution acidic, basic, or neutral? Justify your answer.

<p>Basic: $K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$; in this case $[\text{NH}_3]=[\text{NH}_4^+]$, so $K_a = [\text{H}_3\text{O}^+]$. Thus $\text{pH} = \text{p}K_a$. $\text{p}K_a = -\log K_a = -(-9.26) = 9.26$.</p> <p>or</p> <p>$K_b$ for the weak base is larger than K_a for the weak acid, so the solution must be basic.</p>	<p>One point is earned for indicating that $\text{pH} = \text{p}K_a$.</p> <p>One point is earned for correct choice based on correctly calculating or noting the value of pH.</p> <p>NOTE: Be consistent if K_a calculated in part (e) is larger than K_b.</p>
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- (ii) Calculate the pH of the solution that would result from adding 0.0200 mol of HCl to the solution. Assume that the addition of the HCl does not change the volume of the solution.

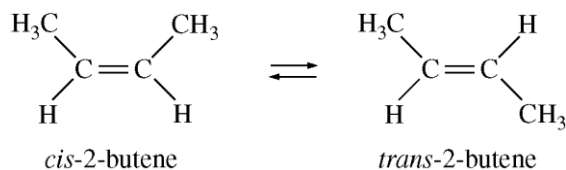
	$\text{NH}_3(aq)$	$+$	$\text{H}^+(aq)$	\rightleftharpoons	$\text{NH}_4^+(aq)$	
I	0.0160		0.0200		0.0160	
C	-0.0160		-0.0160		+0.0160	
E	0		0.0040		0.0320	
	$[\text{H}_3\text{O}^+] = (0.0040)/(0.040) = 0.10\text{M}$; $\text{pH} = 1.00$					

One point is earned for correct calculation of moles or concentration of reactants *prior* to reaction.

One point is earned for correct numerical value of pH.

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Question 7
(4 points)



The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

For a first-order reaction, the half-life is independent of reactant concentration (or pressure) at constant T , as shown in trials 1, 2, and 3.

1 point is earned for a correct explanation.

(b) Calculate the rate constant, k , for the reaction at 350. K. Include appropriate units with your answer.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100. \text{ s}} = 0.00693 \text{ s}^{-1}$$

1 point is earned for correct numerical answer with units.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

The initial rate in trial 1 is less than that in trial 2 because rate = $k[\textit{cis}\text{-}2\text{-butene}]$ or rate = $kP_{\textit{cis}\text{-}2\text{-butene}}$ (with reference to values from both trials).

OR

because the initial concentration of *cis*-2-butene in trial 1 is less than that in trial 2 and k is constant.

1 point is earned for the correct answer with justification.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

The temperature is higher in trial 4, meaning that the KE_{avg} of the molecules is greater. Consequently, in this trial a greater fraction of collisions have sufficient energy to overcome the activation energy barrier, thus the rate is greater.

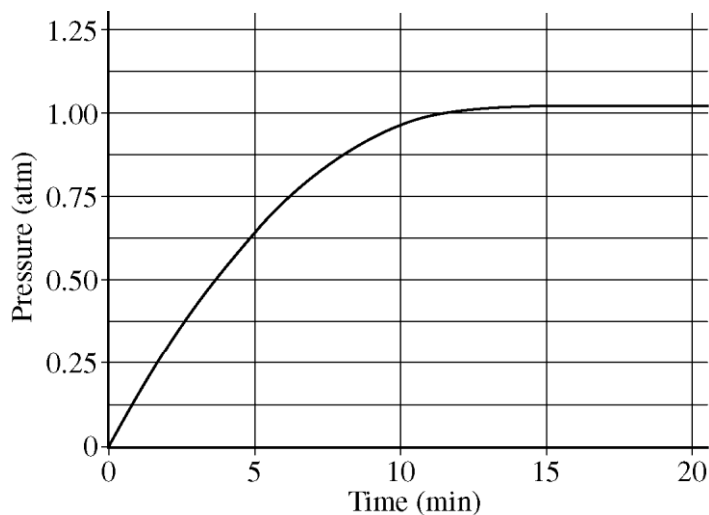
1 point is earned for a correct answer with justification.

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Question 4
(4 points)



When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $\text{CaCO}_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $\text{CO}_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $\text{CaCO}_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

(a) Calculate the number of moles of $\text{CO}_2(g)$ present in the container after 20 minutes of heating.

$PV = nRT$ $\frac{PV}{RT} = n = \frac{(1.04 \text{ atm})(1.00 \text{ L})}{(0.0821 \frac{\text{L atm}}{\text{mol K}})(1100 \text{ K})} = 0.0115 \text{ mol CO}_2$	1 point is earned for the proper setup using the ideal gas law and an answer that is consistent with the setup.
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Question 4 (continued)

- (b) The student claimed that the final pressure in the container in each experiment became constant because all of the $\text{CaCO}_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.

<p>Do not agree with claim</p> <p>Explanation I: In experiment 1, the moles of $\text{CaCO}_3 = 50.0 \text{ g}/100.09 \text{ g/mol} = 0.500 \text{ mol CaCO}_3$. If the reaction had gone to completion, 0.500 mol of CO_2 would have been produced. From part (a) only 0.0115 mol was produced. Hence, the student's claim was false.</p> <p>Explanation II: The two different experiments (one with 50.0 g of CaCO_3 and one with 100.0 g of CaCO_3) reached the same constant, final pressure of 1.04 atm. Since increasing the amount of reactant did not produce more product, there is no way that all of the CaCO_3 reacted. Instead, an equilibrium condition has been achieved and there must be some solid CaCO_3 in the container.</p>	<p>1 point is earned for disagreement with the claim <u>and</u> for a correct justification using stoichiometry or a discussion of the creation of an equilibrium condition.</p>
--	--

- (c) After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.

<p>The final pressure would be equal to 1.04 atm. Equilibrium was reached in both experiments; the equilibrium pressure at this temperature is 1.04 atm. As the reaction shifts toward the reactant, the amount of $\text{CO}_2(g)$ in the container will decrease until the pressure returns to 1.04 atm.</p>	<p>1 point is earned for the correct answer with justification.</p>
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- (d) Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p , for the decomposition of $\text{CaCO}_3(s)$ at 1100 K? Justify your answer.

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Question 4 (continued)

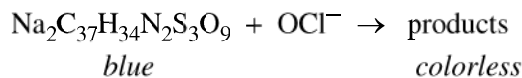
Yes. For the equilibrium reaction represented by the chemical equation in this problem, at a given temperature the equilibrium pressure of CO_2 determines the equilibrium constant. Since the measured pressure of CO_2 is also the equilibrium pressure of CO_2 , $K_p = P_{\text{CO}_2} = 1.04$.

Note: If the response in part (b) indicates “yes”, that all of the $\text{CaCO}_3(s)$ had decomposed, then the point can be earned by stating that the system did not reach equilibrium in either experiment and hence the value of K_p cannot be calculated from the data.

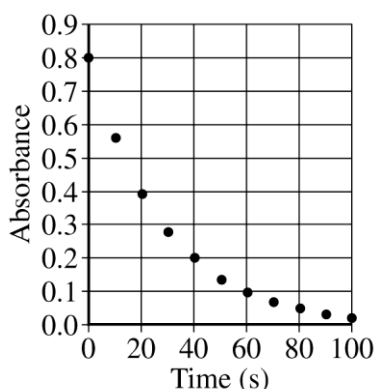
1 point is earned for correct explanation that is consistent with the student’s answer to part (b).

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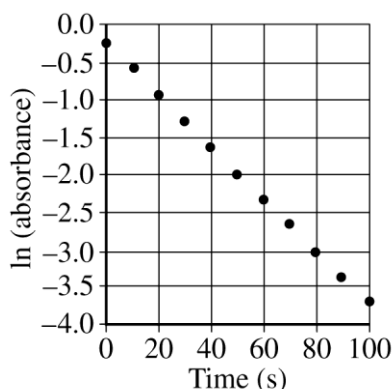
Question 5



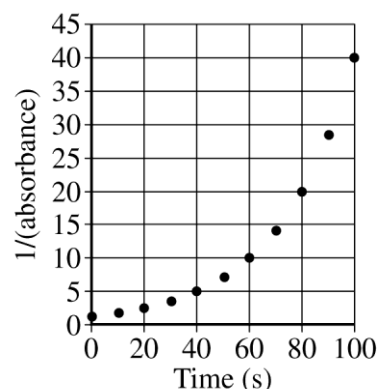
Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I



Graph II



Graph III

(a) Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?

First order	1 point is earned for the correct order.
-------------	--

(b) The reaction is known to be first order with respect to bleach. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

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Question 5 (continued)

<p>["Increasing the concentration of the food coloring" should be circled.]</p> <p>If the initial concentration of blue food coloring is increased, then more time is required (regardless of the reaction order indicated in part (a)) for the bleach to oxidize the additional blue food coloring.</p>	<p>1 point is earned for the correct choice.</p> <p>1 point is earned for a correct explanation.</p>
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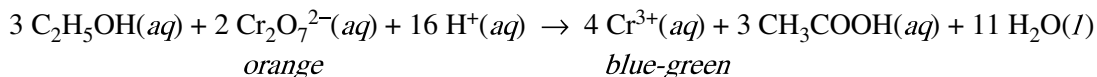
- (c) In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?

<p>The spectrophotometer should be set to a different wavelength.</p>	<p>1 point is earned for a correct answer.</p>
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Question 1 (continued)

An alternative approach to determine the concentration of $\text{C}_2\text{H}_5\text{OH}(aq)$ in a solution is based on the reaction represented below.



A solution has an initial $\text{Cr}_2\text{O}_7^{2-}(aq)$ concentration of $1.0 \times 10^{-3} M$ and an initial $\text{C}_2\text{H}_5\text{OH}(aq)$ concentration of $0.500 M$. The solution contains enough strong acid to keep the pH essentially constant throughout the reaction. The student places a sample of the solution in a cuvette that has a path length of 0.50 cm and places it in a spectrophotometer set to measure absorbance at 440 nm . ($\text{Cr}_2\text{O}_7^{2-}(aq)$ is the only species in the reaction mixture that absorbs light at this wavelength.) The absorbance of $\text{Cr}_2\text{O}_7^{2-}(aq)$ in the solution is monitored as the reaction proceeds; the table below shows the absorbance as a function of time for the first trial.

Time (min)	Absorbance at 440 nm
0.00	0.782
1.50	0.553
3.00	0.389
4.50	0.278
6.00	0.194

(d) Calculate the value of $[\text{Cr}_2\text{O}_7^{2-}]$ at 1.50 min.

<p>Absorbance is proportional to $[\text{Cr}_2\text{O}_7^{2-}]$.</p> $\frac{1.0 \times 10^{-3} M}{0.782} = \frac{x}{0.553}$ $x = 7.1 \times 10^{-4} M$ <p>OR</p> <p>Initial condition: $a = \frac{A}{bc} = \frac{0.782}{(0.50 \text{ cm})(1.0 \times 10^{-3} M)} = 1564 M^{-1} \text{ cm}^{-1}$</p> <p>At 1.50 min: $c = \frac{A}{ab} = \frac{0.553}{(1564 M^{-1} \text{ cm}^{-1})(0.50 \text{ cm})} = 7.1 \times 10^{-4} M$</p>	<p>1 point is earned for the correct concentration.</p>
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Question 1 (continued)

- (e) The student runs a second trial but this time uses a cuvette that has a path length of 1.00 cm. Describe how the experimental setup should be adjusted to keep the initial absorbance at 0.782. Justify your answer with respect to the factors that influence the absorbance of a sample in a spectrophotometer.

$A = abc$ If path length (b) is doubled, and molar absorptivity (a) is constant, the initial concentration of $\text{Cr}_2\text{O}_7^{2-}$ (c) must be halved to keep the initial absorbance (A) constant.	1 point is earned for reference to a factor that affects absorbance. 1 point is earned for the correct adjustment.
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For the concentrations of reactants used in the experiment, the rate of the reaction can be written as follows.

$$\text{Rate} = k_{\text{observed}}[\text{Cr}_2\text{O}_7^{2-}]^y, \text{ where } k_{\text{observed}} = k[\text{C}_2\text{H}_5\text{OH}]$$

- (f) Explain how the experimental data indicate that the reaction is first order with respect to $\text{Cr}_2\text{O}_7^{2-}$.

Absorbance is proportional to concentration of $\text{Cr}_2\text{O}_7^{2-}$. Absorbance is halved after 3.00 min and again after another 3.00 min. Thus the half-life of the reaction is constant, so the reaction must be first order with respect to $\text{Cr}_2\text{O}_7^{2-}$. OR Demonstration that the rate of change in $\ln(A)$ over time is constant.	1 point is earned for a correct explanation that uses the data.
--	---